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Zeolite filled PDMS/PAN membranes for separation of low concentrated alcohol/water mixtures

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Introduction

When lignocellulosic biomass is used for alcohol production (2nd generation bio ethanol and higher order alcohol) the alcohol content derived by fermentation is relatively low, typically below 5 wt%. Due to the high water content much energy is needed for the concentration of alcohol by distillation. A possible alternative for the thermal separation step is pervaporation with organophilic membranes. Zeolite membranes on ceramic tubular supports were developed [1] which are characterized by high fluxes, high selectivity and high thermal resistance. High processing costs of zeolite membranes are resulting high investment costs. For low temperature application zeolite filled polymeric membranes with high filling degree may be an economic alternative. A defined range of particle size distribution allows high silicalite contents in a hydrophobic polymeric matrix like polydimethylsiloxane (PDMS) for mixed-matrix-membranes (MMM). The desired MMM with high filling degrees and functionalized particle surfaces should combine a high permeability and selectivity.

Experimental

Two methods were chosen to get the desired particles: Hydrothermal synthesis of nano (HTN) and micro particles (HTM) and grinding of commercial powders to a defined particle diameter. For further processing it was necessary to transform the suspensions into dry powders. A drying in furnace results in heavy agglomerated products. A special technique of Spray Freeze Drying (SFD) produces free-flowing powders.

To higher the adsorption capacities of organophilic compounds the particle surface was hydrophobized by reaction with polysilanes. These zeolites were deeply investigated in particle morphology, porosity and adsorption properties. The particle morphology was examinated by SEM and laser diffraction. The porosity and pore size distribution were obtained from nitrogen sorption experiments. The adsorption capacities were tested with liquid sorption experiments which were compared with the adsorption in a saturated vapor atmosphere. Liquid sorption experiments were proceeded by adding zeolite powders to defined liquid mixture of 1-butanol/water and heating at 60 °C for 24 h. Afterwards the suspended particles were separated by a filtration and a centrifugation. The water/butanol concentrations of the supernatant liquid were determined by density measurement. For comparison the identic powders were exposed to a saturated butanol atmosphere in a closed vessel for one week. The adsorbed butanol was detected by a thermogravimetric analysis.

For membrane preparation porous PAN substrates were prepared by dissolving polyacrylnitrile in dimethylformamide to form a 11 wt% dope solution which was cast onto the surface of the non-woven fleece and immersed into water to induce polymer precipitation. The resulting PAN ultrafiltration membrane was washed in hot water and dried in an air stream of 60 °C for 5 min. The thickness of the single PAN layer was controlled in the range of 100 – 200 µm determined by scanning electron microscopy (SEM).

For MMM preparation zeolite powder and PDMS added into tetrahydrofuran. For a **homogeneous and bubble-free mixture the suspension was treated by a laboratory mixing system "speedmixer".** The highly viscous suspension was cast onto the PAN porous substrate directly. The composite membrane was dried at room temperature for several hours

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and then placed in furnace at 100 °C to remove the residual solvent and polymerize the polysiloxane. To characterize the polymer as well as the polymer-zeolite compound free standing non-supported membranes were prepared by casting on stainless steel plates and removing of the film after polymerization.

Membranes were characterized by separation experiments (pervaporation (PV)) in low concentrated ethanol/water and butanol/water mixtures at 40°C and 60°C respectively.

Results

All freeze dried products were able to be redispersed in differend solvents. By HTN-methode particle sizes of 40 nm to 80 nm and by HTM average particle diameter of 1 µm to 1.5 µm were synthesized. With the method of grinding average particle diameters of 350 nm – 450 nm were achieved.

By adsorption tests a lowering of the adsorption capacity by grinding was found. Highest capacity was found for non grinded and HTM powders. Additional hydrophobization influenced the adsorption only slightly.

After testing of different polymers by PV the best polymers were stepwise filled with different MFI zeolite contents of the different powder preparation and modification methods. On free standing membranes of 0.5 mm thickness low fluxes of 0.06 kg/m²h and ethanol concentration of 35 wt% were found for pure PDMS (40 °C, 8 wt% EtOH in feed). Adding of grinded powders prepared without SFD gives membranes of high selectivity (permeate concentration 75 wt%) and increased fluxes in a clear dependence on the zeolite content (Fig. 1 and 2). SFD-powders increased the flux by the factor of 10 up to 1.9 kg/m²h but keeps the selectivity quite low (permeate concentration 35 wt%). Additionally adding HTN powder made it possible to increase the zeolite content in the membrane up to 74 wt% but membrane defects lowered the selectivity.

The best combination of zeolite, silicone and process parameter were chosen to obtain thin films of 50 µm thickness on top of PAN-supports. In comparison to the thick free standing membranes for all thin film MMM an increasing of flux by a factor of 20 and nearly constant separation factor was found giving high flux and high selectivity MMM for ethanol upgrading. One membrane was also tested in butanol/water mixtures (60°C, 1.3 wt% butanol). With a flux of 1.8 kg/(m²h) and a permeate concentration of 38 % an interesting starting point for the development of butanol selective membranes is given.

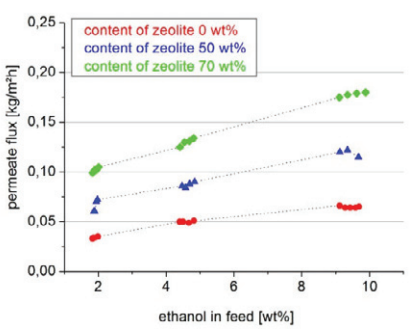

Fig. 1: Permeate flux of free standing MMMs with differend zeolite contents (PV, 40 °C)

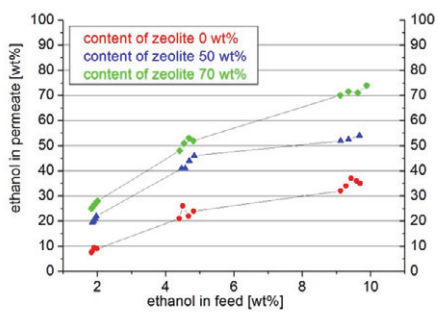

Fig. 2: Permeate concentration of free standing MMMs with differend zeolite contends (PV, 40°C)

Keywords: mixed matrix membrane, zeolite, pdms, pervaporation